

PROBING THE REACTIONS OF ALKYL PEROXYL RADICALS IN THE GAS PHASE USING DISTONIC RADICAL ANIONS

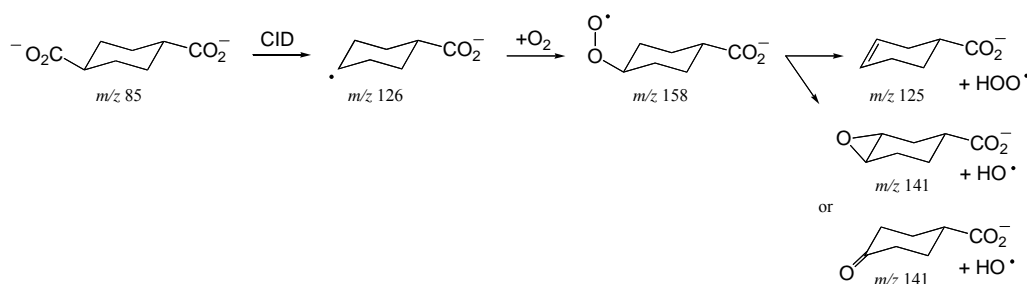
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Alkyl peroxy radicals are known to be reactive intermediates in many crucial chemical processes ranging from lipid peroxidation, to combustion and the generation of photochemical smog. Despite being central to these many chemistries, alkyl peroxy radicals have presented a challenge to the experimentalist as their highly reactive and short lifetimes often defy attempts to isolate and characterize them. Distonic radical anions¹ – where the charge and radical are centred on different atoms in the same molecule – can be readily synthesized and isolated in the gas-phase by mass spectrometry and have been shown to model the reaction pathways of their neutral radical analogues. We have previously demonstrated a method for the synthesis and isolation of adamantyl peroxy radicals using a combination of electrospray ionisation and ion-trap mass spectrometry.² In the present study this approach is expanded to include less structurally rigid hydrocarbon structures in an effort to provide better models for simple alkyl peroxy radicals.

1,3- and 1,4-cyclohexanedicarboxylic acid have been used to prepare the 3- and 4-carboxylatocyclohexyl radical anions. These species were isolated and allowed to react with advantageous oxygen within the ion-trap mass spectrometer forming 3- and 4-carboxylatocyclohexylperoxy species. Fragmentation of these hitherto uncharacterised radicals by collision induced dissociation yields products (*e.g.*, Scheme 1) consistent with those predicted by computational studies on neutral alkyl peroxy radicals.³ The 3- and 4-carboxylatocyclohexyl species present an exciting potential to be used in further ion/molecule experiments as models of alkyl radical reactivity. The most recent unimolecular and bimolecular reactions of these charged alkyl peroxy radicals will be presented.

Scheme 1.



References:

1. Yates, B. F.; Bouma, W. J.; Radom, L., *J. Am. Chem. Soc.* **1984**, 106, 5805.
2. Harman, D. G.; Blanksby, S. J., *Chem. Commun.* **2006**, 8, 859.
3. Rienstra-Kiracofe, J. C.; Allen, W. D.; Schaefer III, H. F., *J. Phys. Chem.* **2000**, 104, 9823.